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DURVILLDIOL AND DURVILLONOL: STRUCTURE AND OCCURRENCE

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Key Word Index—*Pseudocyphellaria*; Stictaceae; triterpenoids; durvilldiol; durvillonol.

Abstract—The triterpenoids durvilldiol and durvillonol, isolated in earlier studies from the lichen *Pseudocyphellaria berberina*, syn. *P. durvillei*, are identified as stictane-3β,22α-diol and 22α-hydroxystictan-3-one respectively.

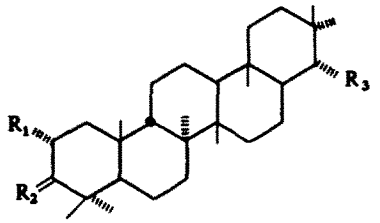
INTRODUCTION

From the extractives of the South American lichen *Pseudocyphellaria berberina* (G. Forst.) D. Gall. *ined.*, syn. *P. durvillei* (Del.) Wain., Huneck and Follman [1] isolated two saturated pentacyclic triterpenoids of unknown structure, one of which was determined to be a ketol and the other a diol. These metabolites which were designated durvillonol and durvilldiol respectively, have been reported [2] to occur, together with zeorin (hopane-6α,22-diol) and other unidentified triterpenoids, in a number of other South American *Pseudocyphellaria* lichens.

RESULTS AND DISCUSSION

On extraction of an authentic specimen of *P. berberina* three triterpenoids were extracted, including a ketol and a diol, which were presumed to be the durvillonol and durvilldiol of Huneck and Follman [1]. Whilst the melting point of the ketol, mp 216–218°, closely resembled that previously reported [1] for durvillonol (mp 218–220°), that of the diol, mp 283–284°, was found to be some 20° higher than that previously reported [1] for durvilldiol (mp 264–266°). This revision prompted a comparison of durvillonol and durvilldiol with 22α-hydroxystictan-3-one (**1a**) and stictane-3β,22α-diol (**1b**) respectively, two of a new group of ten triterpenoids recently isolated [3] from the New Zealand *Pseudocyphellaria* lichens *P. colensoi* (Bab.) Vain, *P. hirta* (Stirt.) D. Gall and P. James, *ined.*, syn. *P. coronata* Bab., and *P. flavicans* (Hook f. and Tayl.) Vain. In each case direct comparisons (mp and mmp, IR, NMR, MS) substantiated the identities proposed. In addition the third triterpenoid, (which the previous studies [2] appeared to identify with zeorin) was found to be a dihydroxyacetate, $C_{32}H_{54}O_4$, mp 216-218°, IR(nujol) 3580, 3450, 1735, and 1240 cm^{-1}, and identified as 2α-acetoxystictane-3β,22α-diol (**1c**), one of a pair of epimeric dihydroxyacetates also isolated from the New Zealand lichens.

An extensive chemotaxonomic survey [4] has recently confirmed the occurrence, in varying quantities, of the foregoing stictane triterpenoids, and in some cases also the epimeric dihydroxyacetate (**1d**) and triol (**1e**), in other



(**1a**) R_1 = H; R_2 = 0; R_3 = OH
(**1b**) R_1 = H; R_2 = H,β-OH; R_3 = OH
(**1c**) R_1 = OAc; R_2 = H,β-OH; R_3 = OH
(**1d**) R_1 = R_3 = OH; R_2 = H,β-OAc
(**1e**) R_1 = R_3 = OH; R_2 = H,β-OH

South American *Pseudocyphelllaria* lichens, *viz. P. compar* (Nyl.) H. Magn., *P. corulescens* (Mont.) H. Magn., *P. endochrysa* (Del.) Vain, *P. scabrosa* R. Sant. in Lamb, and South American collections of material presently referred to *P. flavicans*. However, these specimens possess a triterpenoid metabolite pattern different to collections, including type specimens, which originate from New Zealand. These studies have also established that whilst hopane triterpenoids occur widely in white medulla *Pseudocyphellaria* lichens, the occurrence of stictane triterpenoids is largely, but not uniquely, confined to yellow medulla species, and contrary to the earlier report [2], stictane triterpenoids do not appear to co-occur with hopane triterpenoids.

EXPERIMENTAL

Extraction and isolation of triterpenoids from P. berberina. The finely ground lichen (5.4 g) was extracted in a Soxhlet apparatus with $CHCl_3$ (190 ml) for 18 hr. Evaporation of the solvent gave a residue (188 mg) which was dissolved in Et_2O (200 ml) and washed with 10% aqueous KOH (2 × 100 ml). Separation of the resulting neutral fraction (124 mg) by multiple (× 3) PLC on Si gel with Et_2O–hexane (1 : 1) gave 22α-hydroxystictan-3-one (**1a**) (40 mg), mp and mmp 216–218° (sublimed sample) [4], stictane-3β,22α-diol (**1b**) (16 mg), mp and mmp 283–284° (sublimed sample) [4], and 2α-acetoxystictane-3β,22α-diol (**1c**) (33 mg), mp and mmp 216–218° (sublimed sample) [4]. Each of the foregoing compounds also displayed spectral features (IR, NMR, MS) identical to those previously reported.

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BIOSYNTHESIS OF EUGENOL AND CINNAMIC ALDEHYDE IN *CINNAMOMUM ZEYLANICUM*

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Key Word Index—*Cinnamomum zeylanicum*; Lauraceae; cinnamon; biosynthesis; eugenol; phenylalanine; methionine.

Abstract—Incorporation of [^{14}C]-phenylalanine and [^{14}C]-methionine into cinnamon cuttings suggests that synthesis of eugenol from phenylalanine involves exchange of the terminal carbon in the side chain with that from a donor molecule such as methionine whereas synthesis of cinnamic aldehyde incorporates phenylalanine *in toto*.

INTRODUCTION

Cinnamomum zeylanicum Nees (Cinnamon) produces various oils that are of considerable commercial importance. The major constituent of oil derived from the leaf is eugenol while the major component of stem bark oil is cinnamic aldehyde [1]. The biosynthesis of eugenol and cinnamic aldehyde in cinnamon has not been reported in the literature. Studies on other plant tissues [2–6] have shown phenylalanine to be a precursor of eugenol and cinnamic aldehyde but the reaction sequence involved in the syntheses varies in different tissues. This paper describes the feeding of [^{14}C]-phenylalanine and [^{14}C]-methionine to cinnamon cuttings and the determination of the activity incorporated into eugenol and cinnamic aldehyde.

Table 1. Incorporation of [^{14}C] phenylalanine and methionine into cinnamon leaf oil, cinnamic aldehyde and eugenol after 5 hr feeding through the cut ends of cinnamon cuttings

Precursor	Incorporation (%)		
	Leaf oil	Cinnamic aldehyde	Eugenol
DL-Phenyl-[1-^{14}C]-alanine	0.015	0.009	0.003
DL-Phenyl-[2-^{14}C]-alanine	0.69	0.010	0.047
DL-Phenyl-[3-^{14}C]-alanine	0.86	0.009	0.098
L-[Methyl-^{14}C]-methionine	0.70	0.016	0.092
DL-Phenyl-[3-^{14}C]-alanine + L-[Methyl-^{14}C]-methionine	1.36	0.017	0.12

Values are means of two experiments

RESULTS AND DISCUSSION

Table 1 shows that the incorporation of label from phenyl-[2-^{14}C]-alanine and phenyl-[3-^{14}C]-alanine into eugenol was much greater than that from phenyl-[1-^{14}C]-alanine; and that relatively substantial incorporation occurred from [methyl-^{14}C]-methionine. This suggests that the terminal carbon of phenylalanine is removed during its conversion to eugenol and replaced with a —Me from a donor molecule. Degradation of eugenol derived from incubation with [methyl-^{14}C]-methionine to methyleugenol and oxidation to homoveratric acid cleaves the terminal carbon in the allyl group. Homoveratric acid retained very little activity and confirmed that [methyl-^{14}C]-methionine only contributed to the terminal carbon in the allyl chain (Table 2). It was possible that methionine could have also donated the methyl group for OMe on Carbon-3 in the aromatic ring, but if this had occurred to any extent then homoveratric acid would have retained more activity. A relatively small loss in specific activity occurred in methyleugenol relative to eugenol which was probably due to uncontrolled oxidation of the side chain during the reaction and extraction steps. Table 1 shows that the activity incorporated into cinnamic aldehyde was similar for all forms of phenylalanine, indicating that the whole phenylalanine structure was incorporated into cinnamic aldehyde. The biosynthetic pathway pro-

Table 2. Radioactivity of eugenol, labelled by methionine, during degradation to methyleugenol and homoveratric acid

Compound	Yield (mg)	Total radioactivity (dpm)	Specific activity (dpm/mg)
Eugenol	225	38 850	173
Methyleugenol	200	24 450	122
Homoveratric acid	45	135	3